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A Formal Solution of the Equations of Statistical Equilibrium

BRUNO ZUMINO

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Abstract

A closed expression is given for the distribution functions in the classical theory of statistical equilibrium. This expression, when suitably expanded, permits one to obtain rather simply the general term in the virial expansion of the distribution functions and of the equation of state.

Table of Contents

Page

1. Introduction 1
2. Formal expression for the distribution functions 3
3. Expansion to first order in the density 5
4. Note 6

References 7

Distribution List

1. Introduction

The object of the present note is to give an explicit solution of a system of equations introduced by Bogolubov[1] for the distribution functions in the classical theory of statistical equilibrium. This solution, when suitably expanded, permits one to obtain rather simply the general term in the virial expansion of the distribution functions and of the equation of state. Although our solution is given in closed form, it must be considered as being of formal nature, since it involves operations of differentiation and of substitution of variables to be performed on functionals.

We consider a system of N identical monatomic molecules enclosed in a macroscopic volume V. It will be assumed that both N and V tend to infinity, in such a way that their ratio remains constant

$$(1) \qquad \frac{N}{V} = c.$$

The symmetric distribution functions $F_s(x_1,\dots x_s)$, normalized so that

$$(2) \qquad \lim_{V\to\infty} \frac{1}{V^s} \int_V \cdots \int_V F_s(x_1,\dots,x_s)dx_1\dots dx_s = 1 ,$$

satisfy the infinite system of coupled equations

$$(3) \qquad \frac{\partial F_s}{\partial x_1^\alpha} + \mu \frac{\partial U_s}{\partial x_1^\alpha} F_s + \mu c \int \frac{\partial \Phi(|x_1-x_{s+1}|)}{\partial x_1^\alpha} F_{s+1} dx_{s+1} = 0$$

$$s = 1,2\dots,$$
$$\alpha = 1,2,3.$$

where Φ is the intermolecular potential, $U_s = \frac{1}{2}\sum_{k,\ell}^{s} \Phi(|x_k-x_\ell|)$, $\mu = \frac{1}{kT}$.

The infinite system of equations (3) has been derived by Bogolubov from the customary canonical distribution of Gibbs. An alternative derivation presents some interest, since it may provide an independent foundation for equilibrium statistics. One first obtains, from the Liouville equation, the well-known hierarchy of infinitely many equations for the time-dependent distribution functions[2], [8], [10]. One then seeks time-independent solutions which are Maxwellian in their velocity dependence: for their coordinate dependence the system (3) obtains.

The infinite system (3) is clearly equivalent to a single functional differential equation for the generating functional

$$(4)\qquad F[\chi] = \sum_{s=1}^{\infty} \frac{1}{s!} \int \cdots \int F_s(x_1,\ldots,x_s)\, \chi(x_1)\ldots\chi(x_s)\,dx_1\ldots dx_s$$

from which the distribution functions can be obtained by functional differentiation

$$(5)\qquad F_s(x_1,\ldots,x_s) = \left.\frac{\delta^s F}{\delta\chi(x_1)\ldots\delta\chi(x_s)}\right|_{\chi = 0} .$$

The functional F is defined for test functions χ which tend to zero sufficiently fast at infinity. The equation satisfied by F is*

$$(6)\qquad \frac{\partial}{\partial x^\alpha}\frac{\delta F}{\delta\,\chi(x)} + \mu \int \frac{\partial\phi(|x-y|)}{\partial x^\alpha}\,\frac{\delta^2 F}{\delta\chi(x)\delta\chi(y)}\,(\chi\,(y)+c)dy = 0 .$$

The physically meaningful solution of (3) or (6) is known in the limit $c \to 0$, of zero density**:

$$(7)\qquad F_1^o = 1,\quad F_s^o = e^{-\mu U_s} \qquad s = 2,3,\ldots \quad .$$

The equations can be solved in power series of c, starting from (7) as a zero-order solution. The first few terms have been calculated and shown to

---

* Equations of this type have been considered, e.g., by Bazarov[3].

** Here and in the following we shall simply denote by a superscript zero quantities referring to the zero density limit. They will be related to each other by equations similar to those relating the corresponding quantities without superscript. Thus one has, together with equations (10) and (12) below, the equations

$$F^o = e^{G^o} - 1,\qquad H^o = \frac{\delta G^o}{\partial\,\chi(x)} .$$

Quantities with a superscript zero are considered known.

reproduce the well-known virial expansion*. However, the form of equation (6) suggests that one may obtain a complete solution by taking as independent variable the function

$$(8) \qquad \tilde{\chi}(y) = \chi(y) + c$$

since the equation then reduces to its form for c = 0. This is not quite correct, of course, because $\tilde{\chi}$ is not an admissible test function for F (it does not vanish at infinity); some transformations inspired by the theory of Ursell function must be performed first.

2. Formal expression for the distribution functions

To carry out the transformations mentioned in the preceding section, we introduce a new functional

$$(9) \qquad G[\chi] = \sum_{s=1}^{\infty} \frac{1}{s!} \int G_s(x_1,\ldots,x_s)\, \chi(x_1)\ldots\chi(x_s)\, dx_1\ldots dx_s$$

related to $F[\chi]$ by

$$(10) \qquad F = e^{G} - 1 \,.$$

The functions G_s generated by G are related to the distribution functions F_s in the same way that the customary Ursell functions are related to the Boltzmann factors**

$$(11) \qquad \begin{aligned} F_1(x_1) &= G_1(x_1) \\ F_2(x_1,x_2) &= G_2(x_1,x_2) + G_1(x_1)G_1(x_2) \\ &\;\;\ldots \qquad\qquad \text{etc.} \end{aligned}$$

---

* See the papers quoted in [1] and [3].

** The connection between equations like (10) and (11) has been pointed out before by Mazo and Zemach[4]. These authors also show how (10) can be used to prove quite simply the property of the G_s functions of vanishing for large separation of the arguments, when the F_s functions factorize for large separation.

The equation (6) can be quite easily transformed into an equation for G, or rather, for

$$(12)\qquad H[x,\chi] = \frac{\delta G}{\delta\chi(x)} = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int G_{s+1}(x,x_1,\dots,x_s)\chi(x_1)\dots\chi(x_s)dx_1\dots dx_s \, .$$

It takes the form

$$(13)\qquad \frac{\partial}{\partial x^{\alpha}} H[x, \chi] + \mu \int \frac{\partial\phi}{\partial x^{\alpha}} \left(\chi(y)+c\right)\left(\frac{\delta H[x,\chi]}{\delta\chi(y)} + H[x,\chi]H[y,\chi]\right)dy = 0 \, .$$

The advantage of this transformation is that $\chi + c$ is an admissible test function for $H[x, \chi]$, since the functions generated by H are of the Ursell type, and vanish themselves when the coordinates are far away from x, so that the test function does not have to vanish. The substitution (8) is now permissible. More generally one can easily verify that

$$(14)\qquad H[x,\chi] = \underline{a}\, H^{o}\left[x,\underline{a}(\chi + c)\right]$$

is a solution, $\underline{a}$ being an arbitrary constant.

The constant $\underline{a}$ cannot be chosen equal to unity, since the normalization condition (2) implies that

$$(15)\qquad G_1(x)\left[= F_1(x)\right] = 1$$

and therefore, from (12) and (14), that

$$(16)\qquad \underline{a}H^{o}[x,\underline{a}c] = 1.$$

For the purpose of identification with known results one can show quite easily that the condition (16) for $\underline{a}$ can be written as

$$(17)\qquad \underline{a}\sum_{n=1}^{\infty} nb_n(\underline{a}c)^{n-1} = 1$$

where

$$(18)\qquad b_1 = 1,\quad b_n = \frac{1}{n!}\int H_n^{o}(x_1,x_2\dots x_n)dx_2\dots dx_n \quad n = 2,3,\dots$$

are the well-known cluster integrals[5]. Therefore the product

(19) $$\underline{a}c = z$$

is the activity and (16), or

(20) $$c = zH^{o}[x,z] \; ,$$

expresses the relation between density and activity. Equation (14) can now be written

(21) $$H[x,\chi] = \frac{z}{c} H^{o}\left[x,\frac{z}{c}\chi + z\right] .$$

Equations (9), (12), (20) and (21) together describe the desired solution. The solution appears expressed in terms of the activity z; if one desires an expression in terms of the density, one must first invert equation (20).

3. Expansion to first order in the density

As an example, we shall now use the obtained solution to calculate the distribution function F_2 neglecting terms of second order in the density. From (20)

(22) $$\frac{c}{z} = H^{o}[x,z] = 1 + z \int G_2^{o}(x,x_1)dx_1 + O(z^2).$$

Equation (22) shows that

(23) $$z = c + O(c^2)$$

so that, in the following, we will have to retain only terms of first order in z. Clearly, from (21),

(24) $$G_2(x_1,x_2) = \frac{\delta H[x_1,\chi]}{\delta\chi(x_2)}\bigg|_{\chi = 0} = \left(\frac{z}{c}\right)^2 \frac{\delta H^{o}[x_1,\chi]}{\delta\chi(x_2)}\bigg|_{\chi = z}$$

and

(25) $$\frac{\delta H^{o}[x_1,\chi]}{\delta\chi(x_2)}\bigg|_{\chi = z} = G_2^{o}(x_1,x_2) + z \int G_3^{o}(x_1,x_2,x_3)dx_3 + O(z^2) .$$

Finally, substituting in (24) the results (22) and (25),

$$(26)\qquad G_2(x_1,x_2) = G_2^0(x_1,x_2)\left\{1-c\int G_2^0(x_1,x_3)dx_3-c\int G_2^0(x_2,x_3)dx_3\right\}$$

$$+c\int G_3^0(x_1,x_2,x_3)dx_3+O(c^2).$$

The function F_2 is given by

$$(27)\qquad F_2(x_1,x_2) = G_2(x_1,x_2) + 1$$

It is quite easy to see that the above approximate result agrees with previously given expressions. As it is shown, for instance, in Reference 1, this result can be used to obtain the virial expansion of the equation of state to second order in the density.

Note

The system of integral equations (3) was given independently by Bogolubov[1] and by Born and Green[8]. Closely related integral equations had previously been considered by Yvon[6] and by Kirkwood and Boggs[7]. Mayer[9] also makes extensive use of integral relations between the distribution functions.

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